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13. ABSTRACT (Maximum 200 words) Nanolaminates are multilayered thin film structures with very high interfacial density. These composite multilayer structures can display interesting properties that are not observed in the individual components. These special properties can be optimized by manipulating the thickness and composition of the individual nanolayers. The optimized nanolaminates may have important applications as better protective coatings and thin films with enhanced optical and electrical properties. Our research has focused on the fabrication of nanolaminates with atomic layer deposition (ALD) techniques based on sequential self-limiting surface chemistry. We have also concentrated on measuring the properties of nanolaminates. Our goal has been to grow and characterize metal/ceramic and ceramic/ceramic nanolaminates and to develop design rules for the construction of novel nanocomposite materials. We have utilized the ALD techniques that we have recently pioneered to obtain atomic layer controlled growth. We have utilized our surface chemistry for W ALD and Al ₂ O ₃ ALD to construct W/Al ₂ O ₃ metal/ceramic nanolaminates. We have also used our surface chemistry for ZnO and Al ₂ O ₃ ALD to construct ZnO/Al ₂ O ₃ ceramic/ceramic nanolaminates and alloys. Following the growth of these nanolaminates, we have determined structure/property relationships for nanolaminates.		
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Final Report

Fabrication and Properties of Nanolaminates Using Self-Limiting Surface Chemistry Techniques

AFOSR Grant No. F49620-99-1-0081

January 15, 1999 – November 14, 2002

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Abstract

Nanolaminates are multilayered thin film structures with very high interfacial density. These composite multilayer structures can display interesting properties that are not observed in the individual components. These special properties can be optimized by manipulating the thickness and composition of the individual nanolayers. The optimized nanolaminates may have important applications as better protective coatings and thin films with enhanced optical and electrical properties. Our research has focused on the fabrication of nanolaminates with atomic layer deposition (ALD) techniques based on sequential self-limiting surface chemistry. We have also concentrated on measuring the properties of nanolaminates. Our goal has been to grow and characterize metal/ceramic and ceramic/ceramic nanolaminates and to develop design rules for the construction of novel nanocomposite materials. We have utilized the ALD techniques that we have recently pioneered to obtain atomic layer controlled growth. We have utilized our surface chemistry for W ALD and Al_2O_3 ALD to construct W/ Al_2O_3 metal/ceramic nanolaminates. We have also used our surface chemistry for ZnO and Al_2O_3 ALD to construct ZnO/ Al_2O_3 ceramic/ceramic nanolaminates and alloys. Following the growth of these nanolaminates, we have determined structure/property relationships for nanolaminates.

Outline of Final Report

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I. Introduction

Over the last four years, our research has concentrated on fabrication and properties of nanolaminates using self-limiting surface chemistry techniques. We are interested in nanolaminates because novel material properties occur when structural dimensions reach the nanoscale. These new properties are observed when the material size becomes comparable with the characteristic length scale that defines the bulk material property. Nanolaminates provide an important testbed to vary material thicknesses and tune physical properties. In this research, we have utilized atomic layer deposition (ALD) techniques to fabricate a variety of nanolaminates with novel physical properties.

During our funding period, our work has focused on two important nanolaminate systems: $\text{ZnO}/\text{Al}_2\text{O}_3$ and $\text{W}/\text{Al}_2\text{O}_3$. These two nanolaminates represent two important categories of nanolaminates. The $\text{ZnO}/\text{Al}_2\text{O}_3$ nanolaminate is a ceramic/ceramic nanolaminate. The $\text{W}/\text{Al}_2\text{O}_3$ nanolaminate is a metal/ceramic nanolaminate. Both of these systems are also conductor/insulator nanolaminates because ZnO and W are conductors and Al_2O_3 is an insulator. In addition, these systems are crystalline/amorphous nanolaminates because ZnO and W are both polycrystalline at their deposition temperatures and Al_2O_3 is amorphous.

With these goals and focus in mind, much of our research has been aimed at growing the two nanolaminates, characterizing the nanolaminate structures and understanding the nanolaminate properties. In addition, we have actively sought out collaborations to extend our capabilities and promote our work in industry. This aspect of our work has been very rewarding and we have developed many partnerships during the course of this work. Our goal is to perform important science and engineering. We also have definite products and applications in mind for our research and development effort funded by the AFOSR.

II. Technique and Instrument Development

During our funding period, we worked on improving our abilities to fabricate and evaluate thin films grown using atomic layer deposition (ALD) techniques. The nanolaminate work required that we expand the number of reactant channels on our viscous flow ALD reactor. We built a new 6-channel viscous flow reactor for rapid deposition of Al_2O_3 , ZnO and W and

their nanolaminates. This new 6-channel reactor has been named the "Venice" reactor. The Venice reactor has greatly improved our ability to grow nanolaminates.

We also improved our ability to study ALD and monitor thin film growth in the Venice reactor using an in situ quartz crystal microbalance (QCM). The QCM technique has proven to be a powerful in situ probe of ALD. We have developed a "back side" purge on the QCM that prevents the ALD film from growing on the back side of the QCM sensor. This "back side" purge has enabled the QCM technique to measure absolute growth rates.

We were fortunate to receive a DURIP grant for an x-ray diffractometer two year ago. This x-ray diffractometer has allowed us to perform both x-ray reflectivity (XRR) and x-ray diffraction (XRD) analysis of our thin films. The XRR capability is especially important for the evaluation of our nanolaminate samples. For the electrical characterization of insulating thin films, we also built an electrical workstation for current-voltage (IV) and capacitance-voltage (CV) measurements. This electrical workstation is based on a mercury probe.

We have progressively built a toolset for the fabrication and evaluation of thin films. Combined with an earlier DURIP grant for a scanning probe microscope, we are fairly well equipped for thin film growth and analysis. We still require a technique for elemental analysis. We find ourselves using the XRD for elemental characterization. We are considering a DURIP proposal for x-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES) combined with a depth-profiling capability.

III. ZnO/Al₂O₃ Nanolaminates & Alloys

The growth and characterization of ZnO/Al₂O₃ nanolaminates and alloys was one of the highlights during our funding period. These nanolaminates were grown in our original 3-channel viscous flow reactor. Since ZnO is conducting and Al₂O₃ is insulating, interesting properties were expected for ZnO/Al₂O₃ alloys. We observed that the ZnO/Al₂O₃ alloys varied by more than 18 orders of magnitude in electrical conductivity when we varied the ZnO/Al₂O₃ alloy composition. This wide spectrum of conductivity is important for many thin film electrical applications, such as depositing conducting films in microchannel arrays.

Since ZnO is crystalline and Al₂O₃ is amorphous at their ALD temperatures, interesting changes in surface roughness were expected for ZnO/Al₂O₃ nanolaminates versus the thickness of the individual nanolayers in the bilayer. We determined that we could tune the surface roughness of the ZnO/Al₂O₃ nanolaminate by varying the thickness of the ZnO nanolayer. This tunable surface roughness is important to minimize light scattering in ZnO optical films and to maximize sensitivity in ZnO gas sensors.

Structural characterization of the ZnO/Al₂O₃ nanolaminates was also performed using x-ray reflectivity (XRR) and grazing incidence x-ray diffraction (XRD). Prior to the acquisition of the x-ray diffractometer, these measurements were conducted in collaboration with Prof. David Johnson at the University of Oregon. The XRR measurements revealed extremely pronounced Bragg peaks for the superlattice structure of the ZnO/Al₂O₃ nanolaminate. These measurements illustrated the high degree of conformality that be achieved using ALD techniques.

IV. W/Al₂O₃ Nanolaminates

Our nanolaminate work has also concentrated on W/Al₂O₃ nanolaminates. These metal/ceramic nanolaminates may have potential as thermal barrier coatings, x-ray mirrors and charge injectors. To optimize the growth of W/Al₂O₃ nanolaminates, we have continued to study W ALD. The reaction mechanism of W ALD was explored using quadrupole mass spectrometry to analyze reaction products. We also explored the nucleation and growth during W ALD on Al₂O₃ surfaces and Al₂O₃ ALD on W surfaces using Auger electron spectroscopy. These studies have developed our basic understanding of the fabrication of W/Al₂O₃ nanolaminates.

We have also explored the properties of W/Al₂O₃ nanolaminates. The XRR of the W/Al₂O₃ nanolaminates displayed very high x-ray reflectivity. In fact, our W/Al₂O₃ nanolaminates are competitive with the best x-ray mirrors prepared using sputtering techniques. 64-bilayer W/Al₂O₃ superlattices with a bilayer thickness of ~30 Angstroms displayed an excellent Bragg peak for the Cu K_α line at 1.54 Angstroms. We are currently working with two x-ray companies, Osmic and Bede Scientific, on optimizing the x-ray reflectivity further.

Recent research in collaboration with Prof. David Cahill at the University of Illinois at Urbana has also illustrated the potential of the W/Al₂O₃ nanolaminates as thermal barrier coatings. We grew a set of W/Al₂O₃ nanolaminates with a total thickness of 400 Angstroms with different numbers of bilayers ranging from 2 to 20. The measured thermal conductivity of these samples reduced with increasing interfacial density. These results illustrate that phonon scattering at interfaces can dramatically affect heat transfer through thin films. We are currently evaluating the thermal stability of these W/Al₂O₃ nanolaminates.

V. Personnel Supported

Faculty

1. Prof. Steven M. George (One Month Summer Salary)

Postdoctoral Research Associates

1. Dr. Jeff Elam
2. Dr. Francois Fabreguette

Graduate Students

1. Robert Grubbs
2. Zachary Sechrist

Much of the research over our funding period was conducted by a senior research associate, Dr. Jeff Elam. Prior to Jeff's departure to Argonne National Laboratories in the spring of 2002, Dr. Francois Fabreguette joined the research group and is now leading our laboratory effort. A third-year graduate student, Zachary Sechrist, has also worked with Jeff and Francois. Zach has concentrated on the W/Al₂O₃ nanolaminates. Another graduate student, Robert Grubbs, has concentrated on the nucleation and growth of W ALD on Al₂O₃ surfaces, the reaction mechanism of W ALD using quadrupole mass spectrometry and the nucleation and growth of Al₂O₃ ALD on W surfaces. Robert recently graduated in spring 2003.

VI. Publications

1. J.W. Klaus, S.J. Ferro and S.M. George, "Atomic Layer Deposition of Tungsten Nitride Films Using Sequential Surface Reactions", *J. Electrochem. Soc.* **147**, 1175-1181 (2000).
2. J.W. Klaus and S.M. George, "Atomic Layer Deposition of SiO₂ at Room Temperature Using NH₃-Catalyzed Sequential Surface Reactions", *Surf. Sci.* **447**, 81-90 (2000).
3. J.W. Klaus and S.M. George, "SiO₂ Chemical Vapor Deposition at Room Temperature Using SiCl₄ + H₂O with a NH₃ Catalyst", *J. Electrochem. Soc.* **147**, 2658-2664 (2000).
4. J.W. Klaus, S.J. Ferro and S.M. George, "Atomic Layer Deposition of Tungsten Using Sequential Surface Chemistry with a Sacrificial Stripping Reaction", *Thin Solid Films* **360**, 145-153 (2000).
5. J.W. Klaus, S.J. Ferro and S.M. George, "Atomically Controlled Growth of Tungsten and Tungsten Nitride Using Sequential Surface Reactions", *Appl. Surf. Sci.* **162-163**, 479-491 (2000).
6. S.M. George, J.D. Ferguson and J.W. Klaus, "Atom Layer Deposition of Thin Films Using Sequential Surface Reactions", in *New Methods, Mechanisms and Models of Vapor Deposition*, Mat. Res. Soc. Sym. Proc. **616**, 93-101 (2000).
7. J.W. Elam, C.E. Nelson, R.K. Grubbs and S.M. George, "Nucleation and Growth During Tungsten Atomic Layer Deposition on SiO₂ Surfaces", *Thin Solid Films* **386**, 41-52 (2001).
8. J.W. Elam, C.E. Nelson, R.K. Grubbs and S.M. George, "Kinetics of the WF₆ and Si₂H₆ Surface Reactions During Tungsten Atomic Layer Deposition", *Surf. Sci.* **479**, 121-135 (2001).
9. S.M. George, J.W. Elam, R.K. Grubbs and C.E. Nelson, "Nucleation and Growth During Tungsten Atomic Layer Deposition on Oxide Surfaces", in *Mechanisms of Surface and Microstructure Evolution in Deposited Films and Film Structures*, Mat. Res. Soc. Sym. Proc. **672**, O7.7.1-O7.7.7 (2001).
10. J.W. Elam, M.D. Groner and S.M. George, "Viscous Flow Reactor with Quartz Crystal

Microbalance for Thin Film Growth by Atomic Layer Deposition", *Rev. Sci. Instrum.* **73**, 2981-2987 (2002).

11. J.W. Elam, Z.A. Sechrist and S.M. George, "ZnO/Al₂O₃ Nanolaminates Fabricated by Atomic Layer Deposition: Growth and Surface Roughness Measurements", *Thin Solid Films* **414**, 43-55 (2002).

12. M.D. Groner, J.W. Elam, F.H. Fabreguette and S.M. George, "Electrical Characterization of Thin Al₂O₃ Films Grown by Atomic Layer Deposition on Silicon and Various Metal Substrates", *Thin Solid Films* **413**, 186-197 (2002).

13. J.M. Jensen, A.B. Oelkers, R. Toivola, D.C. Johnson, J.W. Elam and S.M. George, "X-ray Reflectivity Characterization of ZnO/Al₂O₃ Multilayers Prepared Using Atomic Layer Deposition", *Chem. Mater.* **14**, 2276-2282 (2002).

14. J.W. Elam, Z.A. Sechrist and S.M. George, "Atomic Layer Deposition of ZnO/Al₂O₃ Nanolaminates and Alloys: Fabrication and Properties", *Proceedings of CIMTEC 2002*, International Conferences on Modern Materials and Technologies, Florence, Italy, July 14-18, 2002.

25. J.W. Elam and S.M. George, "Growth of ZnO/Al₂O₃ Alloy Films Using Atomic Layer Deposition", *Chem. Mater.* **15**, 1020-1028 (2003).

26. J.W. Elam, D. Routkevitch and S.M. George, "Properties of ZnO/Al₂O₃ Alloy Films Grown Using Atomic Layer Deposition Techniques", *J. Electrochem. Soc.* **150**, G339-G347 (2003).

VII. Presentations

Our AFOSR-supported research has been well presented to the scientific community through invited talks, contributed talks and contributed posters. The PI has been asked to give presentations at a variety of scientific conferences, academic institutions and companies:

PI INVITED TALKS

1. "Atomic Layer Control of Thin Film Growth Using Sequential Surface Reactions", Dept. of Chemistry, Univ. of Utah, Salt Lake City, Utah, February 8, 1999.
2. "Atomic Layer Control of Thin Film Growth Using Sequential Surface Reactions", *Class of 1960 Seminar Speaker*, Dept. of Chemistry, Williams College, Williamstown, Massachusetts, March 12, 1999.
3. "Atomic Layer Deposition of Ultrathin Films Using Sequential Surface Reactions", Seminar to *Seagate Recording Heads Group*, Seagate Technology, Bloomington, Minnesota, July 29, 1999.
4. "Tungsten and Tungsten Nitride Atomic Layer Deposition Using Sequential Surface Reactions", Nanoelectronics Seminar, The Institute of Physical and Chemical Research (RIKEN), Wakao, Saitama, Japan, August 23, 1999.
5. "Tungsten and Tungsten Nitride Atomic Layer Deposition Using Sequential Surface Reactions", Dept. of Electrical and Electronic Engineering, Tokyo Institute of Technology, Tokyo, Japan, August 24, 1999.
6. "FTIR Studies of Tungsten and Tungsten Nitride Atomic Layer Deposition Using Sequential Surface Reactions", Session on Semiconductor Surfaces and Interfaces, *Twelfth International Conference on Fourier Transform Spectroscopy*, Waseda University, Tokyo, Japan, August 26, 1999.
7. "Atomic Layer Deposition of Thin Films and Nanolaminates", X-Ray Diffraction Workshop, Dept. of Physics, University of Colorado, Boulder, Colorado, March 17, 2000.
8. "Atomic Layer Deposition of Tungsten on Oxide Surfaces", Colloid and Surface Chemistry Division Symposium on *Semiconductor Surface Chemistry: Reactions Involving Metals*, 219th American Chemical Society National Meeting, San Francisco, California, March 27, 2000.

9. "FTIR Studies of the Atomic Layer Deposition of Barrier Seeds Using Sequential Surface Reactions", Honeywell, Electronic Materials and Interconnect Solutions Group, Sunnyvale, California, March 28, 2000.
10. "Atomic Layer Deposition of Nitrides, Metals and Oxides Using Sequential Surface Reactions", IBM T.J. Watson Research Center, Yorktown Heights, New York, April 13, 2000.
11. "Atomic Layer Deposition of Thin Films Using Sequential Surface Reactions", Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Canada, April 14, 2000.
12. "Atomic Layer Deposition of Thin Films Using Sequential Surface Reactions", Symposium on *Novel Methods, Mechanisms and Models of Vapor Deposition*, Materials Research Society Meeting, San Francisco, California, April 25, 2000.
13. "Atomic Layer Deposition of Thin Films Using Sequential Surface Reactions", Applied Materials, Santa Clara, California, June 8, 2000.
14. "Atomic Layer Deposition of Ultrathin Films Using Sequential Surface Reactions", Annual Retreat of the *NSF/SRC Engineering Research Center on Environmentally Benign Semiconductor Manufacturing*, Stanford University, Stanford, California, August 9, 2000.
15. "Atomic Layer Epitaxy", 27th Annual Symposium of the Rocky Mountain Chapter of the American Vacuum Society, Arvada, Colorado, August 24, 2000.
16. "Atomic Layer Deposition of Ultrathin Films Using Sequential Surface Reactions", Dept. of Chemistry, University of New Mexico, Albuquerque, New Mexico, September 8, 2000.
17. "Atomic Layer Deposition of Ultrathin Films Using Sequential Surface Reactions", Patten Lecture, Dept. of Chemical Engineering, University of Colorado, Boulder, Colorado, September 19, 2000.
18. "Tungsten Atomic Layer Deposition: Nucleation and Growth on Oxide Surfaces", Thin Films Division Session on *Atomic Layer Deposition*, 47th International Symposium of the

American Vacuum Society, Boston, Massachusetts, October 2, 2000.

19. "Atomic Layer Deposition of Ultrathin Films Using Sequential Surface Reactions", Dept. of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, October 5, 2000.
20. "Atomic Layer Deposition of Thin Films Using Sequential Surface Reactions", Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson Air Force Base, Dayton, Ohio, October 17, 2000.
21. "Atomic Layer Deposition of Ultrathin Films Using Sequential Surface Reactions", Dept. of Chemistry, University of North Carolina, Chapel Hill, North Carolina, November 2, 2000.
22. "Atomic Layer Deposition of Ultrathin Films Using Sequential Surface Reactions", 31st Semiconductor Interface Specialists Conference, Catamaran Resort, San Diego, California, December 9, 2000.
23. "Thin Films Grown Using Atomic Layer Epitaxy Methods for Magnetic Recording Head Manufacturing", University Research Conclave II, Seagate Technology, Bloomington, Minnesota, December 11, 2000.
24. Atomic Layer Deposition of Tungsten on Oxide Surfaces Using Sequential Surface Reactions, Second International Workshop on Oxide Surfaces (IWOX-2), Quail Ridge Inn, Taos, New Mexico, Jan. 16, 2001.
25. "Atomic Layer Deposition of Thin Films Using Sequential Surface Reactions", Dept. of Chemistry, Montana State University, Bozeman, Montana, Jan. 26, 2001.
26. Atomic Layer Deposition of Metallic Films: Tungsten and Titanium Nitride, Second International American Vacuum Society Conference on Microelectronics and Interfaces, Santa Clara, California, Feb. 8, 2001.
27. Atomic Layer Deposition of Al_2O_3 , ZnO and $\text{Al}_2\text{O}_3/\text{ZnO}$ Nanolaminates Using Sequential Surface Reactions in a Viscous Flow Reactor, Session on *Thin Films: Preparation*,

Characterization, Applications, 221st National Meeting of the American Chemical Society, San Diego, California, April 3, 2001.

28. Nucleation and Growth During Tungsten Atomic Layer Deposition on Oxide Surfaces , Session on *Mechanisms of Surface and Microstructure Evolution in Deposited Films and Film Structures*, Materials Research Society Meeting, San Francisco, California, April 19, 2001.
29. "Atomic Layer Deposition of Tungsten Using Sequential, Self-Limiting Surface Reactions", Tungsten Products Division, Novellus Systems, Inc., San Jose, California, April 17, 2001.
30. "Atomic Layer Deposition of ZnO/Al₂O₃ Nanolaminates and Alloys", Core Technologies, Applied Materials, Santa Clara, California, April 17, 2001.
31. "Atomic Layer Deposition Using Sequential, Self-Limiting Surface Reactions", Applied Films Corporation, Longmont, California, October 4, 2001.
32. "Tungsten Atomic Layer Deposition Using Sequential, Self-Limiting Surface Reactions", Dept. of Materials Chemistry, Uppsala University, Uppsala, Sweden, October 18, 2001.
33. "Atomic Layer Deposition of ZnO/Al₂O₃ Nanolaminates and Alloys", Extended UltraViolet Lithography (EUVL) Group, Lawrence Livermore National Laboratory, Livermore, California, December 20, 2001.
34. "Atomic Layer Deposition of Al₂O₃/ZnO Nanolaminates & Alloys", Dept. of Chemistry, Yale University, New Haven, Connecticut, February 5, 2002.
35. "Atomic Layer Deposition of Al₂O₃/ZnO Nanolaminates and Alloys: Fabrication and Properties", 38th Annual Symposium of the New Mexico Chapter of the American Vacuum Society, Wyndham Albuquerque Hotel, Albuquerque, New Mexico, May 15, 2002.
36. "Atomic Layer Deposition Using Sequential, Self-limiting Surface Reactions", Advanced Energy Corporation, Ft. Collins, Colorado, July 9, 2002.

37. "Atomic Layer Deposition of $\text{Al}_2\text{O}_3/\text{ZnO}$ Nanolaminates and Alloys", Surface Engineering with Ceramics, CIMTEC 2002 International Conferences on Modern Materials & Technologies, 10th International Ceramics Conference, Florence, Italy, July 16, 2002.
38. "Atomic Layer Deposition Using Sequential, Self-limiting Surface Reactions", Applied Materials Corporation, Santa Clara, California, August 6, 2002.
39. "In Situ Probing of Atomic Layer Deposition in Viscous Flow Reactors", American Vacuum Society Topical Conference on Atomic Layer Deposition (ALD 2002), Hanyang Institute of Technology, Hanyang University, Seoul, Korea, August 20, 2002.
40. "Atomic Layer Deposition for Thin Film Growth", Analytical Seminar, Dept. of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, September 23, 2002.
41. "Thin Film Growth Using Atomic Layer Deposition", Chemical Physics Seminar, Dept. of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, September 27, 2002.
42. "Thin Film Growth Using Atomic Layer Deposition", Dept. of Chemical Engineering, North Carolina State University, Raleigh, North Carolina, October 7, 2002.
43. " SiO_2 Atomic Layer Deposition Catalyzed by Lewis Bases", The Fifth Baltic Symposium on Atomic Layer Deposition, University of Tartu, Tartu, Estonia, October 24, 2002.
44. "Thin Film Growth Using Atomic Layer Deposition", Corporate Research and Development, The Dow Chemical Company, Midland, Michigan, November 11, 2002.

The PI and other members of the research group have also presented the results of our AFOSR-supported studies as contributed talks or posters at various meetings and conferences:

CONTRIBUTED TALKS

1. "Atomic Layer Deposition of Tungsten Using Binary Reaction Sequence Chemistry", J.W. Klaus, S.J. Ferro and S.M. George, *Symposium on Lasers, Materials and Surfaces*, 41st

Rocky Mountain Conference on Analytical Chemistry, Denver, Colorado, August 2, 1999.

2. "Atomic Layer Deposition of Tungsten Films Studied Using Auger Electron Spectroscopy", J.W. Elam, C.E. Nelson, R.K. Grubbs and S.M. George, *Symposium on Lasers, Materials and Surfaces*, 41st Rocky Mountain Conference on Analytical Chemistry, Denver, Colorado, August 2, 1999.
3. "Nucleation and Growth of Tungsten on SiO₂ During Atomic Layer Deposition Using Sequential Surface Reactions", J.W. Elam, C.E. Nelson, R.K. Grubbs and S.M. George, Surface Science Division Session on *Metals on Oxides*, 46th International Symposium of the American Vacuum Society, Seattle, Washington, October 25, 1999.
4. "Atomic Layer Deposition of Tungsten and Tungsten Nitride Using Binary Reaction Sequence Chemistry", J.W. Klaus, S.J. Ferro and S.M. George, Thin Film Division Session on *Advanced Thin Film Formation Chemistry*, 46th International Symposium of the American Vacuum Society, Seattle, Washington, October 26, 1999.
5. "Using Atomic Layer Deposition to Grow Multilayered Structures on the Nanometer Scale", S.J. Ferro and S.M. George, Rocky Mountain Symposium on Photons and Chemistry, Estes Park, Colorado, November 12, 1999.
6. "Atomic Layer Deposition of Tungsten on Al₂O₃ Studied Using Auger Electron Spectroscopy", R.K. Grubbs, C.E. Nelson, J.W. Elam and S.M. George, *Symposium on Lasers & Materials Chemistry*, 42nd Rocky Mountain Conference on Analytical Chemistry, Broomfield, Colorado, July 31, 2000.
7. "Electrical Characterization of Ultrathin Al₂O₃ Films Grown by Atomic Layer Deposition in a Viscous Flow Reactor", M.D. Groner, J.W. Elam and S.M. George, Thin Films Division Session on *Atomic Layer Deposition*, 47th International Symposium of the American Vacuum Society, Boston, Massachusetts, October 2, 2000.
8. "Growth and Characterization of Al₂O₃/ZnO Nanolaminates and Alloys", J.W. Elam, M.D. Groner, Z.A. Sechrist and S.M. George, *American Vacuum Society Topical Conference on*

Atomic Layer Deposition (ALD 2001), Monterey, California, May 14, 2001.

9. "Nucleation and Growth During Tungsten Atomic Layer Deposition on Oxide Surfaces", R.K. Grubbs, J.W. Elam and S.M. George, *American Vacuum Society Topical Conference on Atomic Layer Deposition* (ALD 2001), Monterey, California, May 15, 2001.
10. "Atomic Layer Deposition of $\text{Al}_2\text{O}_3/\text{ZnO}$ Nanolaminates and Alloys: Fabrication and Properties", J.W. Elam, M.D. Groner, Z.A. Sechrist and S.M. George, Session on *Atomic Layer Deposition for Silicon Devices*, 48th International Symposium of the American Vacuum Society, San Francisco, California, October 31, 2001.
11. "Nucleation and Growth During Tungsten Atomic Layer Deposition on Oxide Surfaces", R.K. Grubbs, J.W. Elam and S.M. George, Session on *Atomic Layer Deposition for Silicon Devices*, 48th International Symposium of the American Vacuum Society, San Francisco, California, October 31, 2001.
12. "Electrical Properties of $\text{Si}/\text{W}/\text{Al}_2\text{O}_3$ Structures Grown by ALD", F.H. Fabreguette, M.D. Groner, Z.E. Sechrist and S.M. George, *International Conference on Solid Films and Surfaces (ICSFS-11)*, Saint Charles, Marseille, France, July 8-12, 2002.
13. "Optimizing the Growth and Properties of $\text{Al}_2\text{O}_3/\text{W}$ Nanolaminates Fabricated Using Atomic Layer Deposition Techniques", Z.A. Sechrist, F.H. Fabreguette and S.M. George, 44th Rocky Mountain Conference on Analytical Chemistry, Hyatt Regency Denver, Denver, Colorado, July 29, 2002.
14. "Nucleation and Growth Chemistry of Tungsten Atomic Layer Deposition on Oxide Surfaces", R.K. Grubbs, J.W. Elam, N. Steinmetz and S.M. George, 44th Rocky Mountain Conference on Analytical Chemistry, Hyatt Regency Denver, Denver, Colorado, July 29, 2002.
15. "Growth and Properties of $\text{Al}_2\text{O}_3/\text{W}$ Nanolaminates Fabricated Using Atomic Layer Deposition Techniques", Z.A. Sechrist, F.H. Fabreguette, O. Heintz and S.M. George, American Vacuum Society Topical Conference on Atomic Layer Deposition (ALD 2002), Hanyang Institute of Technology, Hanyang University, Seoul, Korea, August 19, 2002.

16. "Optimization and Structural Characterization of Al_2O_3 -W Nanolaminates Grown by Atomic Layer Deposition", F.H. Fabreguette, Z.A. Sechrist, O. Heintz and S.M. George, The Fifth Symposium on Atomic Layer Deposition, University of Tartu, Tartu, Estonia, October 25, 2002.

CONTRIBUTED POSTERS

1. "Atomic Layer Deposition of Tungsten Using Sequential Surface Reactions", J.W. Klaus, S.J. Ferro and S.M. George, Gordon Research Conference on *Reactions at Surfaces*, Ventura, California, March 2, 1999.
2. "Atomic Layer Deposition of Tungsten Using Sequential Surface Reactions", J.W. Klaus, S.J. Ferro and S.M. George, 1st International Conference on Advanced Materials and Processes for Microelectronics, San Jose, California, March 15, 1999.
3. "Atomic Layer Deposition of Tungsten and Tungsten Nitride Using Binary Reaction Sequence Chemistry", J.W. Klaus, S.J. Ferro and S.M. George, *Fifth International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures* (ACSIN-5) Aix-en-Provence, France, July 6-9, 1999.
4. "Atomic Layer Deposition of Tungsten Using Binary Reaction Sequence Chemistry", S.J. Ferro, J.W. Klaus and S.M. George, Annual Symposium of the Rocky Mountain Chapter of the American Vacuum Society, Arvada, Colorado, August 26, 1999.
5. "Atomic Layer Deposition of Nanolaminates", S.M. George, Gordon Research Conference on the *Chemistry and Physics of Nanostructure Fabrication*, Tilton College, Tilton, New Hampshire, July 24-25, 2000.
6. "Electrical Characterization of Ultrathin Al_2O_3 Films Grown by Atomic Layer Deposition", M.D. Groner, J.W. Elam and S.M. George, *American Vacuum Society Topical Conference on Atomic Layer Deposition* (ALD 2001), Monterey, California, May 14, 2001.

VII. Collaborations and Transitions

Atomic layer deposition techniques have many useful technological applications. We have had a variety of industrial collaborations. Some of these collaborations have led to direct industrial funding and others have led to in-kind support including equipment donations. Several collaborations have also led to Phase I SBIR funding.

A. Intel Corporation (through the Semiconductor Research Corporation). Intel Corporation is interested in ultrathin TiN diffusion barriers and copper seeds for multilevel backend interconnections. Intel has supported our studies of TiN and Cu ALD. This work was performed, in part, on the Venice ALD reactor that was constructed for our AFOSR research.

B. Applied Materials. Applied Materials is interested in the ALD growth of silicates for gate oxides in MOSFET devices. Applied Materials is funding our studies of the ALD growth and properties of SiO₂/HfO₂ silicates. The SiO₂/HfO₂ silicate ALD is employing our original 3-channel viscous flow reactor that was initially built for our AFOSR research.

C. Advanced Energy. Advanced Energy (Fort Collins, CO) is a maker of power supplies and plasmas sources for the semiconductor industry. Advanced Energy is very interested in plasma ALD. They have provided plasma sources to facilitate our exploration of plasma ALD. One of these plasma sources is currently used on a project that is focused on coating energetic organic materials. This project is sponsored by Eglin Air Force Base.

D. Applied Films. Applied Films (Longmont, CO) is considering the ALD market. As part of their exploration of possible ALD opportunities, we have collaborated on low temperature ALD. The possible applications is coating polymers with enhanced gas diffusion barriers. This collaborative work utilized the viscous flow reactors built for our AFOSR sponsored research.

E. Nanomaterials Research LLC. Nanomaterials Research LLC (Longmont, CO) is a startup focused on various nanotechnologies. We have collaborated with them on an SBIR Phase I program entitled "ALD of Conformal Coatings for Microchannel Plate Modification". This collaboration has utilized the ZnO/Al₂O₃ alloy that we developed in our AFOSR-sponsored research.

F. ITN Energy Systems. ITN Energy Systems (Denver, CO) is a company focused on a variety of energy technologies. We collaborated with them on an STTR Phase I program that concentrated on "Tunnel Barrier Engineering". This collaboration made extensive use of our

ALD reactors to grow Al_2O_3 ALD films and our electrical workstation for IV and CV analysis. This instrumentation was developed by our AFOSR supported research program.

G. Genus Inc. Genus Inc (Sunnyvale, CA) is a provider of equipment for semiconductor fabrication. Genus now concentrates on equipment for ALD. We have worked with Genus on the development of new ALD surface chemistries for the deposition of nitrides, such as AlN . This work utilizes the ALD viscous flow reactors that we have built for our AFOSR-supported research.

H. ALD NanoSolutions. ALD NanoSolutions is a startup founded by the PI and Prof. Al Weimer in the Dept. of Chemical Engineering at the University of Colorado. We received support from ALD NanoSolutions through an STTR Phase I program entitled "ALD of Oxidizer Coatings on Aluminum Nanoparticles to Fabricate SuperThermite Explosives". This research is utilizing the viscous flow ALD reactor design that was developed for our AFOSR-supported research.

I. Cova Technologies. Cova Technologies (Colorado Springs, CO) is a startup focusing on ferroelectric devices. We have collaborated with Cova to use Al_2O_3 ALD as a diffusion barrier in their ferroelectric stacked structures.

In addition to these industrial collaborations, the results from our AFOSR-sponsored research have already been implemented by several American companies. The most notable example is W ALD. We initially developed W ALD to fabricate $\text{Al}_2\text{O}_3/\text{W}$ ceramic/metal nanolaminates for superior thermal barrier coatings. Our W ALD process is now being used in the semiconductor industry for interconnects fabrication. The self-limiting surface chemistry that we developed for W ALD has proven to be very useful to Applied Materials (Sunnyvale, Calif.) and Novellus (San Jose, Calif.) as a W seed for W chemical vapor deposition (CVD). W CVD is used to fill the contact holes in the first level of backend interconnects. This W is deposited on the active electrical contact to the underlying silicon wafer and the TiN diffusion barrier on the SiO_2 insulating layer that defines the contact hole.

W CVD by itself does not well fill the contact hole. However, W ALD prior to W CVD creates an excellent seed layer for W CVD that enables better contact hole filling. Applied Materials and Novellus are both implementing W ALD as a W seed. Applied Materials has

already shipped deposition equipment based on the W ALD process (see the web article at <http://www.appliedmaterials.com/products/ALD.html>). We have applied for a patent for our W ALD process. This patent application is pending approval and we have negotiated with Applied Materials and Novellus regarding intellectual property rights. We are excited to see our W ALD process appear so quickly in semiconductor product development.

IX. Patents

Based on the support from the Air Force Office of Scientific Research, the University of Colorado has applied for a number of patents based on our AFOSR-sponsored research:

The University of Colorado has applied for an official U.S. Patent Application entitled "A Solid Material Comprising a Thin Metal Film on its Surface and Methods for Producing the Same" in April 2000. This patent application covers the W ALD surface chemistry and thin film growth.

The University of Colorado also applied for an official U.S. Patent entitled "SiO₂ Chemical Vapor Deposition at Room Temperature Using a Gas Phase Catalyst". This patent describes a new method to deposit SiO₂ at low temperatures. This low SiO₂ deposition temperature is important for depositing on thermally fragile organic, polymer or biological substrates.

The University of Colorado has also filed a provisional patent entitled "High Reflectivity and Ultra-High Flux X-Ray Optic Element Based on a Graded Multilayer Inside a Monocapillary Tube Fabricated Using Atomic Layer Deposition Techniques". This new disclosure presents new ALD methods to fabricate superior x-ray mirrors. This x-ray mirror is based on the W/Al₂O₃ nanolaminate.

Based on our collaboration with investigators in the Dept. of Mechanical Engineering, the University has also filed a provisional patent entitled Atomic Layer Deposition on Micro-Mechanical Devices . This provisional patent describes the uses of atomic layer deposition for

the enhancement of MEMS reliability and MEMS performance. This patent uses many of the ALD surface chemistries developed by our AFOSR research.

In addition, another provisional patent entitled Al_2O_3 Atomic Layer Deposition to Enhance the Deposition of Hydrophobic or Hydrophilic Coatings on Micro-Electro-Mechanical Devices is currently being reviewed by the Technology Transfer Office at the University of Colorado. This patent draws heavily from our AFOSR-supported research on Al_2O_3 ALD. This provisional patent should be submitted in the next few months.

X. Honors/Awards

Prof. Steven M. George has received a two year Creativity Award from the National Science Foundation (2002). Prof. George is a fellow in the American Vacuum Society (Fall 2000). He is also a fellow in the American Physical Society (1997). Prof. George has also received the Presidential Young Investigator Award (1988-1993), the Alfred P. Sloan Foundation Award (1988), an IBM Faculty Development Award (1988), a Dupont Young Faculty Awardee (1988), a Dreyfus Award for Newly Appointed Faculty in Chemistry (1985) and an AT&T New Faculty Award (1985).